THERMAL CHARACTERIZATION OF AGAR ENCAPSULATED IN TiO_2 SOL-GEL.

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ABSTRACT

Thermal effusivity evolution as a function of time of emulsions, made of agar encapsulated in TiO_2 matrix synthesized by the sol-gel method, is monitored during dehydration at ambient conditions. Measurements of thermal effusivity were performed by the photoacoustic technique, using a conventional cell. The results show sigmoidal growth as a function of time during the dehydration process. The data analysis show that samples prepared at higher pH values, present an increase in the characteristic dehydration time and a decrease in the velocity of the process.

INTRODUCTION

Encapsulation of biomaterials inside of sol-gel ceramic matrices has received a great attention in order to get a media for storing living microorganisms. However these microorganisms must have a friendly environment in order to survive. One of the most interesting approaches is the use of agar as the host material.

Agar comprises a family of cell-wall polysaccharides extracted from marine algae (Rhodophyte). Agar is a hydrophilic substance that has been extensively used as a gellification agent in food and in other applications in microbiology, biochemistry and biomolecular biology. The ability to form reversible gels simply by cooling hot aqueous solutions is the most important property of agar and can be regarded as the prototype and model for all gelling systems. On the other hand, the sol-gel method offers new possibilities for incorporating biologically active agents within ceramic xerogels at room temperature [1-5]. Sol-gel encapsulation improves the stability of the biomaterial and favors the interactions between the immobilized bio-system and the substrate. Furthermore, the sol-gel method offers many advantages due to its easy preparation characteristics, such as a constant pH level, low temperature, pore size control, etc. [6-7].

The encapsulated biomaterials present a combination of properties of the biological and the inorganic elements that can lead to new technological applications. For example, sol-gel titania is a well known photocatalyst that has been used in widespread environmental applications, because it efficiency to promote reactions leading to the partial or total destruction of organic pollutants. If titania is used to encapsulate a biological component, like some microorganisms or agar, this biomaterial can present the ability to degradate additional biological compounds, or to improve the photodegradation properties of titania [8].

Determination of thermal properties is a useful tool in the study of materials and processes. In the last twenty five years, the photoacoustic (PA) techniques have proven to be a valuable method for the thermal characterization of a wide range of solids [9]. The versatility of these techniques are based on the fact that they look directly at the heat generated in a sample, due to non-radiative de-excitation processes, following the absorption of the modulated light that impinges upon the sample. In particular, the microphone PA techniques are based on the PA effect, which consists on the sound generation produced by pressure changes in the PA gas chamber due to a modulated heating.

The PA techniques in liquids have been widely used in the determination of thermal properties in liquids [10, 11]. Recently it has been shown that the restriction of optical transparency can be surpassed, if a variant of the conventional PA cell is used. In this case, the thermal effusivity can be determined for all kind of liquids [10].

In this paper the thermal characterization of a material composed of encapsulated agar in titania sol-gel matrix, is performed. It is shown that the dehydration process can be followed by monitoring the thermal effusivity as a function of time. It is also shown that the process obeys a second order kinetics. The fit of the experimental results, provides the characteristic time and velocity of these processes.

EXPERIMENTAL ARRANGEMENT

In order to prepare the titania matrix mixed with agar, by the sol gel method, a solution of *Gracilarea cornea* was previously prepared, using 4 g of agar diluted into 40 mL of distilled water [12]. Sol gel titania was produced mixing titanium (IV) n-butoxide (Strem Chemicals 98%) and distilled water in a 1:8 relationship. The mixture was kept at low stirring and room temperature (27°C), with a pH level of 7.0. Aftewards, 20mL agar solution was added drop by drop and the mixture was aged during 22 h until gellation. After the gel was formed, it was dried into a rotary evaporator system (Eseve D402-2) at ambient temperature, eliminating water and alcoxide residues. To make a sample with a pH = 7.5, 1mL of ammonium hydroxide (Baker 28%) was added.

PA monitoring was carried out using the PA cell shown in Fig. 1(a). In this configuration the PA cell is closed, at the bottom end, by a glass window and at the top end, by a removable substrate. An electret microphone is used, coupled to the cavity wall, to sense the pressure fluctuations in the PA chamber produced by the periodic heating of the substrate, due to the pumping beam. This substrate is used as a reference material. The sample is deposited on the external surface of this reference material. The experimental arrangement consists of a He-Ne 25 mW laser beam, which is mechanically modulated by an optical chopper (SR540) at constant frequency (f = 7 Hz), for all experiments, and focused onto the reference. The microphone signal is fed into a lock-in amplifier (SR830), from where the output signal amplitude is recorded, as a function of time, in a personal computer. All measurements were performed using an aluminum foil of 50 μm thickness as the reference material, with a thermal diffusivity of 0.9 cm^2/s.

According to the Rosencwaig and Gersho model [9], the PA signal is determined by the temperature fluctuation, θ, at the air-substrate interface (x = 0). Solving the thermal diffusion equation for the configuration shown in Fig. 1(b), the quotient between the PA signal with sample (θ) and without sample (θ_0) is given by [10]:

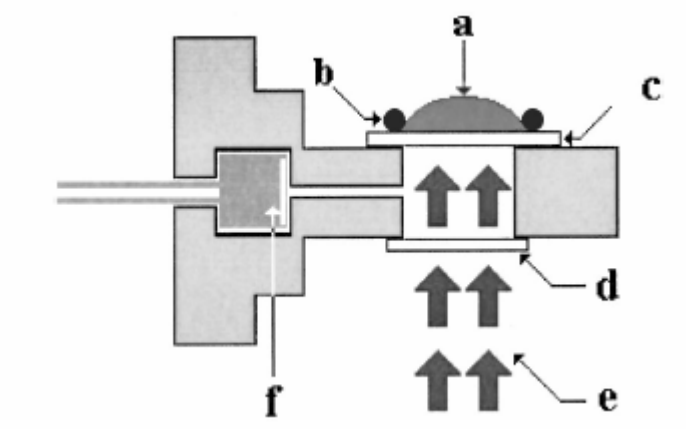

Figure 1. Cross section of the photoacoustic cell used: a) sample, b) 1cm acrylic ring, c) aluminum reference material, d) quartz window, e) modulated light, and f) microphone.

$$q = \left|\frac{\theta}{\theta_0}\right| = \frac{\sqrt{\cosh(2al) - \cos(2al)}}{\sqrt{\cosh(2al) + \cos(2al)}} \frac{\sqrt{(b+1)^2 e^{2al} + (b-1)^2 e^{-2al} - 2(b^2-1)\cos(2al)}}{\sqrt{(b+1)^2 e^{2al} + (b-1)^2 e^{-2al} + 2(b^2-1)\cos(2al)}}. \quad (1)$$

here, $a=(\pi/f\alpha)^{1/2}$, $b = \varepsilon_b / \varepsilon$, is the thermal coupling coefficient, with ε and ε_b the thermal effusivities of the substrate and sample, respectively. It is considered that the thermal effusivity of air is much smaller than the thermal effusivity of the substrate, which is

optically opaque. Solving Eq. (1) for the thermal coupling coefficient, the thermal effusivity of the emulsion can be obtained as a function of time.

The samples to be studied were prepared mixing 2:1 (%wt) of water and powdered sample. The mixture was homogenized during 30 minutes in an ultrasonic bath and an emulsion was obtained. This was deposited on the 1 cm acrylic ring, which is on top of the PA chamber, as shown Figure 1. All experiments were performed at room temperature.

RESULTS

In Figure 2, the photoacoustic signal as a function of time for three different samples is shown: Fresh titania xerogel (FS) and titania-agar samples at two different pH 7 and pH 7.5.

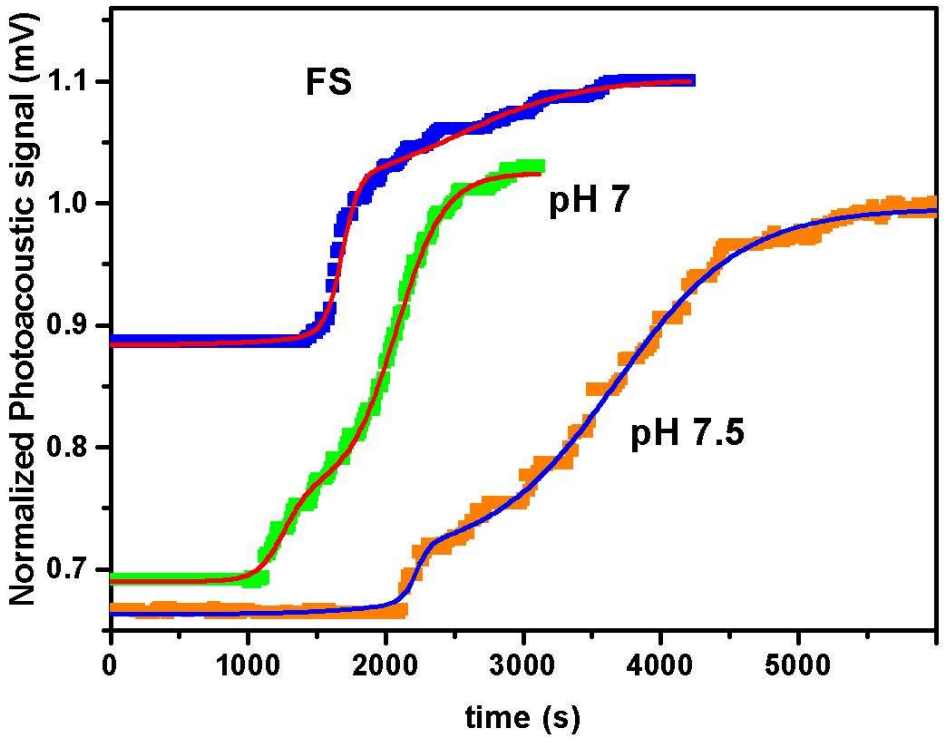

Figure 2. Normalized photoacoustic signal as a function of time for different pH values. Continuous lines correspond to the double sigmoidal fits of the experimental data.

The results will be analyzed using double sigmoidal fitting functions of the following form [10]:

$$\varepsilon_b = A + \frac{B}{1 + e^{(t - t_0)/t_d}}, \qquad (2)$$

where ε_b is the thermal effusivity of the emulsion, t_d is related to the time interval where the maximum variation in the effusivity occurs and t_0 is identified as the time at which the concavity of the sigmoid curve changes. A and B are constants related with the maxima and minima of the signals.

The results are shown in Table 1. The behavior of the material is strongly affected by the presence of agar. The characteristic times t_o for the first and t_{op} for the second sigmoidal, are reduced at low pH values and increased for higher pH values, respectively. On the other hand, settle-down time intervals t_d for the first and t_{pd} for the second sigmoidal, are similar between pH 7.5 and fresh samples. The double sigmoidal behavior is a consequence of two different dehydration processes. The first would be related to water not strongly bounded within the structure of the xerogel, the second part of the dehydration process would imply a behavior related to the hidrophylicity of the materials. These could help us to understand the delayed evaporation process for samples of higher pH values.

Sample	**t_o(s)**	**t_{op} (s)**	t_d **(s)**	t_{pd}	ε_p **(Ws $^{1/2}$/cm^{2}K)**
Titania xerogel	1681	2538	60	437	0.085
Agar-Titania pH = 7	1258	2073	94	176	0.095
Agar-Titania pH = 7.5	2222	3675	51	462	0.095

Table 1. Characteristic time intervals and thermal effusivity for the different samples.

In Figure 3, the thermal effusivity of the same samples can be observed, for all of them the two bumps behavior is present; however for the fresh sample is more pronounced. For the analysis of the thermal effusivity of agar-titania samples, the process will be considered as happening as a whole process obeying only a single sigmoidal. The characteristic times t_e, where the processes reach their maximum velocity are 2000 s for pH-7 and 4000 s for pH 7.5, showing that the increase in alkalinity slows down the whole dehydration process. This behavior is also observed for the settle-down time that is 465 s at pH 7.5 and 193 s at pH 7.

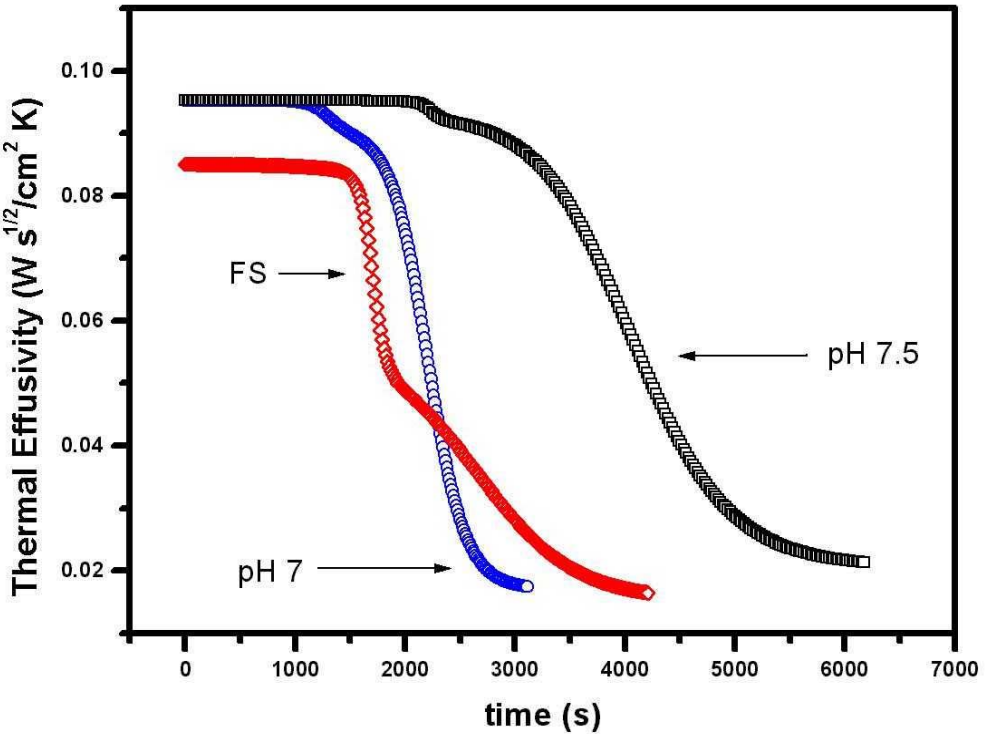

Figure 3. Calculated thermal diffusivity as a function of time for different pH values and for the titania sol-gel matrix without encapsulated agar.

In relation to the fact, that these curves show initially a stationary behavior during a well-defined period of time, these response is related to the thermal diffusion length of the different samples. Given that the samples contain an important quantity of water at the beginning of the process, it can be considered that the effective thermal diffusivity of the samples is near $\alpha \approx 0.0015\ cm^2/s$[8]. At the modulation frequency of 7 *Hz*, the thermal diffusion length would be about $\mu = 80\mu m$. As a consequence of this, using our approach, it is only possible to analyze the process occurring at this length. The observed difference in the initial time, are therefore due to factors related to the thermal diffusivity of the samples, but it will also be strongly influenced by the dehydration rate.

This can be understood taking into account that, due to the migration of species intralayer and interlayer through oxygen lattice framework for forming new phases, and due to dehydroxylation during the thermal treatment; some special structural defects may be created in different phases, particularly, in the case of the catalysts prepared by using sol-gel technique because of the presence of many hydroxyls in the structure at the stage of the gel formation [8].

CONCLUSIONS

Thermal effusivity of the dehydration process of emulsions of encapsulated agar in titania sol-gel ceramic matrix, has been studied. The monitoring was performed using conventional photoacosutic techniques. It has been shown that this methodology is strongly sensitive in the analysis of the different process of dehydration occurring in the samples. In particular has been shown that increasing in pH during the preparation process, strongly influences the rate of dehydration as well as settle-down time intervals. This will be helpful in the understanding of the interaction and hydrophylicity of the matrix and agar, that it is a decisive factor influencing the usefulness of these materials as hosting structures for their use in encapsulation of microorganisms.

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